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Research on the Exploration of Methods to
Produce Chlorates and Perchlorates by Means
Other Than Electrolytic

PART II

INTERIM RESEARCH REPORT

for

Office of Naval Research

CONTRACT NONR 682 (OO)

November 30, 1952



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MATHIESON CHEMICAL CORPORATION

BALTIMORE, MARYLAND

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Research on the Exploration of Methods to Produce Chlorates
and Perchlorates by Means Other Than Electrolytic

INTERIM REPORT FOR PERIOD JUNE 1, 1952 to NOVEMBER 30, 1952

PART II

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Research on the Exploration of Methods to Produce
Chlorates and Perchlorates by Means Other Than Electrolytic

I. OBJECTIVE

It was our purpose to develop a process utilizing dilute ozone as the oxidant to convert a chlorine-containing compound to perchlorate. This oxidant ranks close to fluorine as the most powerful oxidizing agent in acid solution. Now that dilute ozone sells for approximately ten cents (\$0.10) per pound, (1) we intended to develop a process using this cheap, powerful oxidant.

II. SUMMARY

(1) A new reaction has been found for producing perchlorates from chlorates utilizing ozone as the oxidant.

(2) Runs have been made using ozone to oxidize chlorate dissolved in concentrated perchloric acid. The single pass yields (based on NaClO_3 and O_3) were both found to be over 85% (Run 4D) at a NaClO_3 flow of 76 millimoles per hour.

(3) No perchlorate was produced using lead dioxide and lead tetracetate as catalysts with ozone in different solvent media.

(4) Future studies will cover complete laboratory developments of ozone as an oxidant to produce perchlorate from chlorate. All laboratory data will be completed to make possible a preliminary cost estimate by the engineering department for this process.

III INTRODUCTION

The work covered by this experimental investigation can be divided into two major parts:

- (A) The reaction between dilute ozone and chlorate in a concentrated mineral acid over a range of temperatures.
- (B) The reaction between dilute ozone and chlorate with catalysts in the absence of concentrated mineral acids.

The first part of the work proved to be successful, and a complete process is now being developed.

Reactions investigated under (B) yielded no perchlorates and this part of the experimental work was discontinued when part (A) reaction proved successful.

IV. EXPERIMENTAL PREPARATION OF PERCHLORATESA. By Reaction of Dilute Ozone on Chlorate in Concentrated Mineral Acid(1) General Theoretical Perspective

There are many conflicting reports in the literature on the oxidation of chlorate to perchlorate by ozone. These are summarized in a literature report by the Pennsylvania Salt Manufacturing Company (2) and in an interim report issued by Mathieson Chemical Corporation (3) on the perchlorate problem. In the former report the conclusion is drawn that the oxidation of chlorate to perchlorate by ozone may be possible but would be very inefficient.

The Pennsylvania Salt Manufacturing Company did some experimental work on the oxidation of chlorate with ozone. These results are listed in Part II of their report (4). In the summary of this report it was stated: "Ozone failed to oxidize either an alkaline or acid solution of sodium chlorate." We investigated the action of ozone on chlorate in basic solution and reached the same conclusion, that there was no conversion to perchlorate. This work is reported in our Interim Research Report for period December 1, 1951 to May 31, 1952 (3).

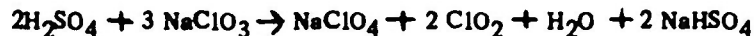
The present report discusses our results on the ozonolysis of salts in acid solution. The work was divided into two general categories:

- (a) The action of ozone on chlorate in concentrated mineral acid.
- (b) The action of ozone on chlorate with catalysts in the absence of concentrated mineral acid.

We shall report the work of ozone on chlorate in concentrated mineral acid first, as this proved to be the most fruitful line of attack.

(2) Chlorate in 25% and 60% Perchloric Acid

It is possible to produce some perchlorate from chlorate in strong acid by simple acid conversion. This is illustrated by the following equation:



Here all of the oxidizing action comes from the chlorates. In the above equation only 33% of the NaClO_3 becomes NaClO_4 . In our reactions we attempted to use ozone as the oxidizing agent. Therefore any conversion over this 33% would indicate that ozone is taking over as the oxidant.

Below in Table I are listed the first experiments using perchloric acid as the solvent with chlorate in solution. The ozone stream was a mixture of 1.0% ozone in oxygen.

Table 2 lists the results of a series of experiments using dilute ozone on sodium chlorate in perchloric acid. The first series of experiments, numbers, 2A, 2C, 2D and 2O were run in a column packed with one-quarter inch Berl saddles. In Experiment 2D we obtained approximately maximum yields for this column on a NaClO_3 flow of 76 millimoles NaClO_3/hr . In this experiment both the single pass yield (based on NaClO_3) and single pass yield (based on O_3) were over 85%. This is plotted in Figure 2.

The second series of experiments listed in Table 2 were run in about the same manner, using a column packed with 4 mm Berl saddles. The smaller packing material has the effect of lengthening the reactor column which should give higher ozone efficiency and conversion to perchlorate. This was found to be true and is confirmed in experiment 4D, where a single pass yield (based on NaClO_3) of 86.0% and a single pass yield (based on O_3) of 88.3% were obtained on a NaClO_3 flow of 76 millimoles NaClO_3 per hour. These experiments are plotted in Figure 3.

It is possible that even higher conversions and ozone efficiencies could be obtained by improved column design, but this can be carried out much more effectively in the pilot plant. This process will be continuous in its operation and in Figure 4 the process is outlined in a preliminary flow sheet.

This reaction is new, and therefore the mechanism of the reaction is not fully understood. However in our experiments we observed that chlorine dioxide is liberated and it appears to aid in obtaining high conversion to the perchlorate. This condition is brought about by having high temperature (100°C .) in conjunction with the presence of concentrated mineral acid. One possible mechanism for this conversion to perchlorate is presented below.

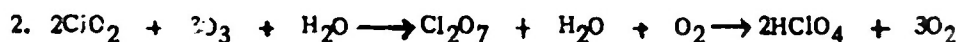
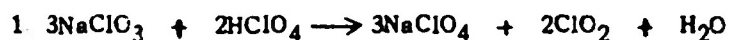
TABLE II
EXPERIMENTS WITH OZONE ON SODIUM CHLORATE IN 60%

PERCHLORIC ACID IN PACKED COLUMN

Exp. No.	Temp. in Reactor	Reactor Column Measurements	Solution	Grams Ozone per hr.	Grams NaClO ₃ per hr.	Millimoles NaClO ₃ /hr.	% NaClO ₃ Unreacted	% NaClO ₃ Destroyed, etc.	% Single Pass Yield (Based on NaClO ₃ charged)	% O ₃ Unreacted	% O ₃ Destroyed, etc.	% Single Pass Yield (Based on O ₃ charged)
2A	100°C	17.5" L. x 1" diam., 139 gr Berl Saddles (1/4" Size, Vol. 200 cc.)	4.0% Solution of NaClO ₃ in 59.84% HClO ₄	3.60	3.53	33.1	5.5	0.0	94.5	58.0	0.0	42.0
2C	100°C			3.70	1.93	18.1	2.6	0.0	97.4	77.0	0.0	23.0
2D	100°C			3.77	8.18	76.8	12.5	2.7	84.8	13.6	3.4	83.0
2O	100°C			3.79	11.92	111.8	26.4	4.6	69.0	2.6	0.0	97.4
4C	100°C		4.0% Solution of NaClO ₃ in 59.21% HClO ₄	3.70	11.05	104	22.0	6.2	71.8	3.5	0.0	96.5
4D	100°C			3.60	8.14	76.4	11.2	2.8	86.0	7.5	4.2	88.3
4G	100°C			3.70	5.21	48.8	11.60	0.0	88.4	40.3	2.7	57.0

* Weight Percent Ozone in Gas = 7.6

† Theoretical Flow of NaClO₃ = 76 Millimoles/hr.NOTE: % Single Pass Yield = $\frac{\text{NaClO}_4 \text{ Formed}}{\text{NaClO}_3 \text{ or O}_3 \text{ Charged}}$



Equation number 3 points out the fact that one oxygen atom from the ozone is attached to the sodium chlorate molecule to form sodium perchlorate.

(3) Chlorate in 65% Sulfuric Acid

The two other mineral acids studied besides perchloric acid for use as solvent were sulfuric acid and nitric acids. Sulfuric acid appears to be equally as good as concentrated perchloric acid for a solvent in this ozone reaction. The experiments using sulfuric acid as solvent are listed in Table 3.

In experiment 41F a conversion of 72.0% was obtained in a packed tower. It is probable that higher yields would have been obtained if precipitation of potassium perchlorate on the column had been avoided. Further work was not carried on with this solvent because of the difficulty of eliminating sulfate contamination from the perchlorate product. In the field of solid propellants the sulfate ion is one of the impurities that cannot be tolerated in the perchlorate product.

(4) Chlorate in 70% Nitric Acid

The third and final mineral acid used in this investigation was nitric acid. This acid appears to be an excellent solvent in this process of converting chlorate to perchlorate, using ozone as the oxidant.

The only two experiments done in this solvent are listed in Table III. In experiments 34 and 35 the chlorate was dissolved in the nitric acid and placed in a reactor. Ozone gas (diluted with oxygen) was bubbled through the liquid. This reactor was heated externally while the gas was on stream. In experiment 35 a conversion of 90.8% of the chlorate to perchlorate was obtained. Nitric acid has definite possibilities as a solvent in this ozone process. Here also as with H_2SO_4 the possible draw back is impurity in the perchlorate due to nitration contamination. However, according to a representative of the Bureau of Aeronautics, trace impurities of nitrate ion can be tolerated.

TABLE III
EXPERIMENTS WITH OZONE ON CHLORATE IN H_2SO_4

AND IN HNO_3

Exp. No.	Temp. in Reactor	Reactor Type	Time Hr.	Gram Moles of Chlorate	Gram Moles of Solvent	Gram Moles of Water	Gram Moles of Ozone	Gram Moles of Oxygen	% Conversion Chlorate to Perchlorate
34	80-115°C	Berch	6.0	$KClO_3$ 0.122	HNO_3 2.5	3.75	0.65	18.1	79.1
35	20-112°C	Berch	1.33	$NaClO_3$ 0.047	HNO_3 1.33	2.0	0.14	4.03	90.8
41A	100°C	Packed Tower 1/4" Berl Saddles	1.0	$KClO_3$ 0.014	H_2SO_4 0.56	1.6	0.035	0.71	72.0
41F	100°C	Packed Tower 1/4" Berl Saddles	1.0	$KClO_3$ 0.028	H_2SO_4 1.14	3.2	0.035	0.71	*72.0
41D	100°C	Packed Tower 1/4" Berl Saddles	1.0	$KClO_3$ 0.029	H_2SO_4 1.17	3.3	0.077	1.5	*58.0

* Washings of tower after these two runs yielded 0.682 gr. of $KClO_4$. This would explain low conversions.

B. Reaction of Dilute Ozone on Chlorate with Catalyst in the
Absence of Concentrated Mineral Acids

(1) General Theoretical Perspective

The oxidation of chlorate to perchlorate can be completed by using lead dioxide as oxidant. This work was reported by the Germans (5) who developed a workable process during World War II. The process is being tested in our laboratory at the present time. This process converts the PbO_2 to $PbSO_4$.

We are carrying on catalyst studies (3) at the present time on the conversion reaction of chlorate to perchlorate. The two catalysts studied recently and reported here are lead salts, namely lead dioxide and lead tetracetate. These two salts were used as catalysts in the reaction of ozone on chlorate in different solvents. These catalysts were planned to function as a bridge to bring the oxygen atoms in the ozone into union with chlorate to form perchlorate. The results of these experiments are discussed in the sections that follow.

(2) Lead Dioxide as Catalyst

Work was carried on with ozone as the oxidant and PbO_2 as the catalyst with chlorate in dilute solutions. Actual experimental conditions are listed below in Table 4. In none of the experiments listed was perchlorate produced. This phase of the work was discontinued once the ozone on chlorate in concentrated mineral acid was found to produce perchlorate in high yield.

TABLE IV
EXPERIMENTS WITH OZONE ON CHLORATE WITH LEAD DIOXIDE AS CATALYST

Exp. No.	Temp.	Time Hr.	pH	Grams Ozone Per Hour	Grams PbO ₂ Catalyst	Grams NaClO ₃	Grams of Solvent	Grams NaClO ₃ Recovered	Remarks
21A	25°C	3.0	Neutral	0.85	1.00	2.00	H ₂ O	1.99	No Perchlorate
23A	25°C	3.0	1.1	0.85	0.50	2.00	0.077N H ₂ SO ₄	2.00	No Perchlorate
24A	25°C	2.0	10.8	0.85	0.50	2.00	0.1005N NaOH	1.99	No Perchlorate
25A	25°C	3.0	1.1	0.85	0.10	2.00	0.077N H ₂ SO ₄	1.98	No Perchlorate

(3) Lead Tetracetate as Catalyst

Lead tetracetate is also an oxidizing agent in acid solution as is lead dioxide. Experiments were run attempting to use lead tetracetate as a catalyst in varying concentrations of acetic acid with dilute ozone as the oxidant. The results of these experiments are listed below in Table 5. None of these experiments gave a detectable amount of perchlorate under the conditions used.

During the course of these runs, the lead tetracetate tended to hydrolyze in the presence of water and precipitate lead dioxide. Here also as in the case of the lead dioxide catalyst, the work was dropped once successful results were obtained using ozone on chlorate in concentrated mineral acid to produce perchlorate.

TABLE V
EXPERIMENTS WITH OZONE ON CHLORATE WITH LEAD TETRACETATE AS CATALYST

Exp. No.	Temp.	Time Hr.	pH	Grams Ozone Per Hour	Grams $Pb(C_2H_3O_2)_4$ Catalyst	Grams $NaClO_3$	Grams of Solvent	Grams $NaClO_3$ Recovered	Remarks
27A	25°C	3.0	Constant	0.85	0.50	2.00	$HC_2H_3O_2$ 50 Gr	1.91	$NaClO_3$ and $Pb(C_2H_3O_2)_4$ not in solution
28A	25°C	2.33	0.58	0.85	0.50	2.00	80% $HC_2H_3O_2$ 50 Gr	1.90	Some PbO_2 PPT.
30A	25°C	5.0	0.93	0.85	0.50	2.00	70% $HC_2H_3O_2$ 50 Gr	1.97	No Perchlorate Some PbO_2 PPT.
29A	25°C	3.0	1.42	0.85	0.50	2.00	50% $HC_2H_3O_2$ 50 Gr	2.00	No Perchlorate Some PbO_2 PPT.

V. CONCLUSIONS

(1) A chemical process using ozone to produce perchlorates has been found and has possibilities of competing economically with present electrolytic production.

(2) This chemical process converts chlorate to perchlorate in concentrated mineral acid solution using ozone as the oxidant.

(3) Lead dioxide and lead tetracetate proved unsuccessful as catalyst, under the conditions used, in converting chlorate to perchlorate.

(4) At present there are not enough data available to construct a working pilot plant for perchlorate production using ozone as the oxidant. Future work will obtain this information.

VI. FUTURE WORK

(1) Experimental work should be completed on the ozone process for conversion of chlorate to perchlorate. This will make possible a preliminary cost estimate on the process. The following information will be obtained:

- (a) Phase diagram of system $\text{NaClO}_3 - \text{NaClO}_4 - \text{HClO}_4(60\%)$
- (b) Vapor pressure studies, at different temperatures, of 60% HClO_4 solution saturated with NaClO_4 .
- (c) Densities of process liquors.
- (d) Cyclic bench scale operating data to confirm optimum conditions.

(2) Pilot plant operation of process

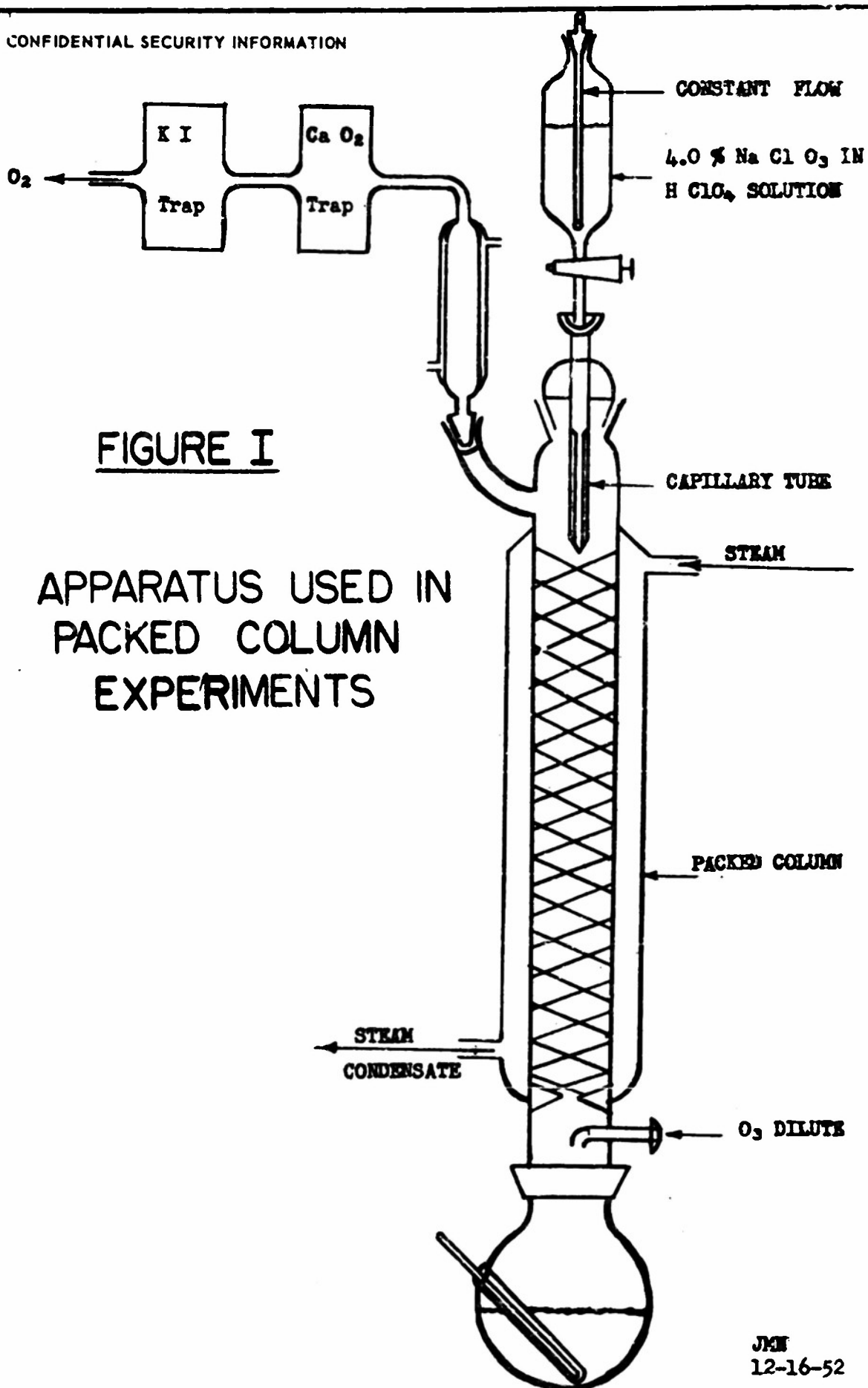
(3) Further exploratory work on the ozonolysis of other chlorine compounds such as HCl , Cl_2O , Cl_2 and HOCl

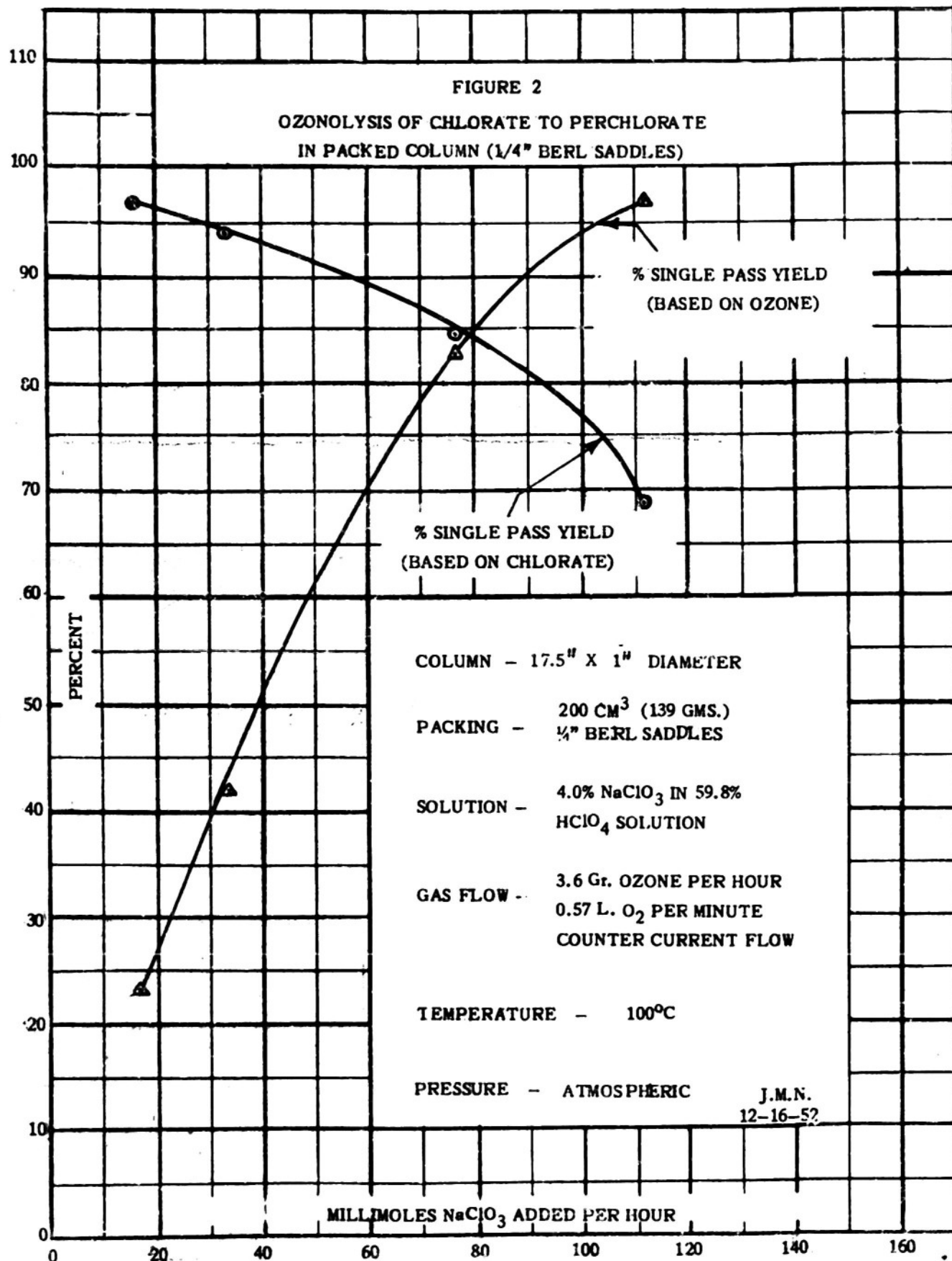
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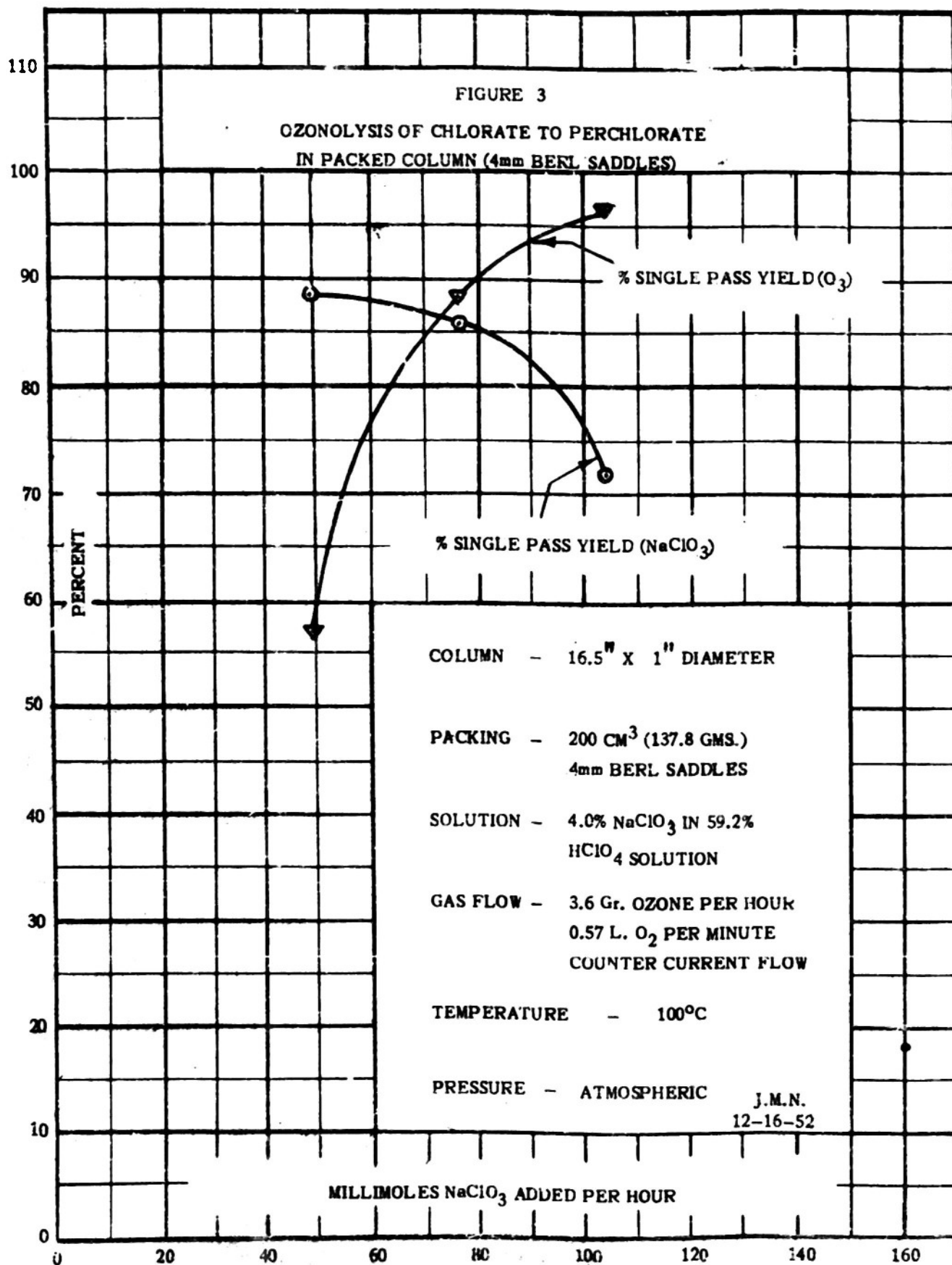
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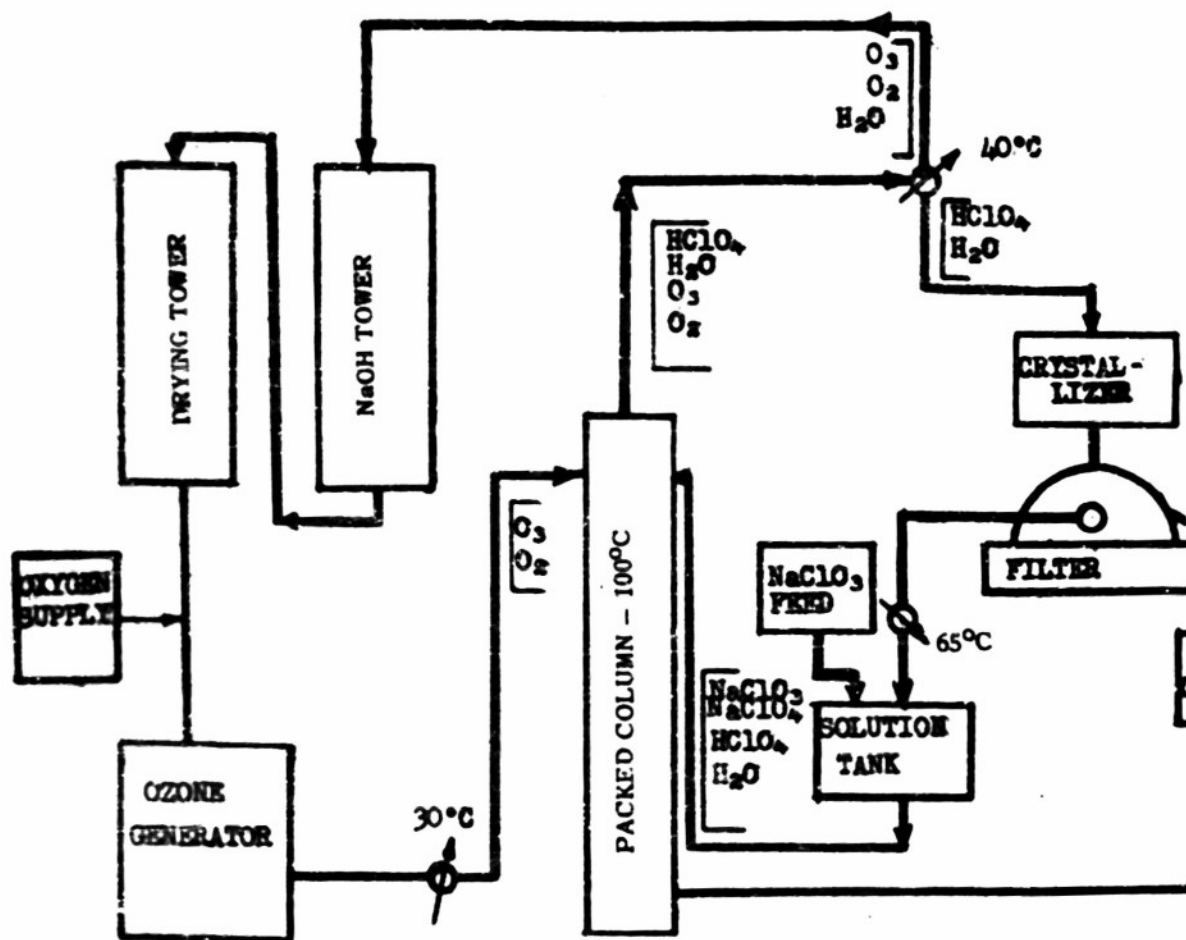


FIGURE 4- FLOW DIAGRAM OF PERCHLORATE PROCESS USING OZONE AS OXIDANT